

Unusual Isomerization of Ortho-Chelated Aryliridium(I) Complexes, Involving a Unique Sequence of Intramolecular C-H Bond-Making and -Breaking Processes. X-ray Structure of $\text{Ir}^{\text{I}}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,4}](\text{COD})$

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The reaction of $\text{Li}_n[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2-R-6}]_n$ with $[\text{IrCl}(\text{COD})]_2$ yields the ortho-chelated aryliridium(I) complexes $\text{Ir}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2-R-6}](\text{COD})$ ($\text{R} = \text{CH}_2\text{NMe}_2$ (4), Me (5), H (6); COD = 1,5-cyclooctadiene). In solution complexes 4 and 5 isomerize irreversibly at 60 °C to $\text{Ir}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2-R-4}](\text{COD})$ (7 and 8, respectively). The mechanism of this conversion involves the initial intramolecular oxidative addition of one of the NMe C-H bonds, succeeded by a unique sequence of highly regiospecific C-H bond-breaking and -making processes. The solid-state structure of 7 was determined by an X-ray diffraction study. Crystals are monoclinic of space group $C2/c$ with $Z = 8$ and lattice parameters $a = 23.829$ (2) Å, $b = 11.667$ (2) Å, $c = 13.725$ (1) Å, and $\beta = 93.43$ (1)°. The structure was refined to $R = 0.026$ for 3087 observed reflections. The structure of 7 consists of an iridium(I) center that is square planar coordinated by the two double bonds of COD and by the monoanionic aryl ligand through an aromatic C atom and the N atom of the 2- CH_2NMe_2 group.

Introduction

The study of the activation of C-H bonds has become an important topic in organometallic chemistry. Although intermolecular activation of arenes and alkanes by transition-metal complexes is now the focus of much attention,¹ intramolecular activation (cyclometalation) has received the major interest in the past.² In general the latter process is more accessible, since there is a more favorable entropy contribution to the free energy of activation. The oxidative addition of a C-H bond usually requires a highly unsaturated metal center, and therefore mechanistic studies on this process have often involved 16- or, moreover, 14-electron, d^8 metal complexes of rhodium(I), iridium(I), or platinum(II).^{1a}

In a previous paper we reported on the syntheses of the reactive compounds $\text{Rh}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2-R-6}](\text{COD})$ ($\text{R} = \text{CH}_2\text{NMe}_2$ (1), Me (2), H (3); COD = 1,5-cyclooctadiene),³ which are square-planar, four-coordinate, 16-electron complexes in the solid-state (see Figure 1, X-ray structure of 1). In solution, however, 1 and 2 are found to be fluxional, as a result of severe steric crowding between the 6-substituent of the aryl group and a neighboring double bond of COD. The fluxional process involves rupture of the Rh-N bond, rotation around Rh-C(aryl), and re-formation of a Rh-N bond (see Figure 2). Despite the intermediacy of a T-shaped three-coordinate, 14-electron species, 1 and 2 are thermally stable in solution up to +105 °C and neither intra- nor intermolecular addition of C-H bonds was observed. As iridium complexes are generally known to be more reactive in this context than rhodium ones,^{1a} we have also examined the iridium analogues of 1-3. Our results on the syntheses and characterization of these species, as well as their involve-

ment in very unusual intramolecular C-H activation processes, are the subject of this paper.

Experimental Section

General Data. $[\text{IrCl}(\text{COD})]_2$ was prepared according to ref 4. Solvents were carefully dried and distilled prior to use. The reactions were performed under an atmosphere of dry nitrogen by using Schlenk techniques. The ^1H , ^2H , and ^{13}C NMR spectra were recorded on Bruker AC100 and WM250 spectrometers. Elemental analyses were carried out at the Analytical Department of the Institute for Applied Chemistry, TNO, Zeist, The Netherlands.

Synthesis of $\text{Ir}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}](\text{COD})$ (4). A solution of $\text{Li}_2[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}]_2$ was prepared by adding *n*-BuLi (2.4 mL of a 1.35 M solution in hexane) to a solution of 2,6-(Me_2NCH_2)₂ $\text{C}_6\text{H}_3\text{Br}$ (0.88 g, 3.24 mmol) in hexane (5 mL). This solution was added at 0 °C to a suspension of $[\text{IrCl}(\text{COD})]_2$ (0.79 g, 1.18 mmol) in hexane (10 mL) and stirred for 1 h at that temperature. The reaction mixture was filtered at 20 °C, and the residue was extracted with hexane until the initially red extracts were almost colorless (50 mL). The combined filtrate and extracts were evaporated to dryness, and the residue was washed twice with cold (-50 °C) pentane (20 mL), affording orange 4 in 90% yield.

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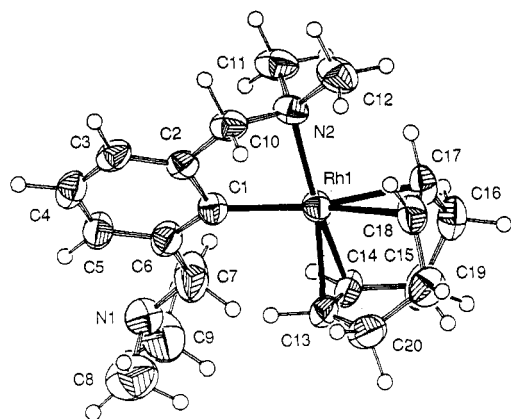


Figure 1. X-ray structure of $\text{Rh}^1[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}](\text{COD})$ (1).³

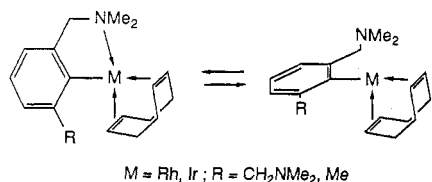


Figure 2. Dynamic behavior of 1, 2, 4, and 5 in solution.

Synthesis of $\text{Ir}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2-Me-6}](\text{COD})$ (5). To a solution of 1-Me-2-Br-3-(Me_2NCH_2) C_6H_3 ³ (0.45 g, 2.0 mmol) in benzene (5 mL) was added 1 equiv of *n*-BuLi in hexane. The solution of the resulting aryllithium compound was added in 2 h at 10 °C to a solution of $[\text{IrCl}(\text{COD})]_2$ (0.60 g, 0.89 mmol) in benzene. The red reaction mixture was subsequently filtered and the filtrate evaporated to dryness. The residue was washed with a little pentane and dried in vacuo, affording orange 5 in 85% yield.

Synthesis of $\text{Ir}[\text{C}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2](\text{COD})$ (6). A benzene solution of $\text{Li}_4[\text{C}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2]_4$ (0.47 g, 0.84 mmol) was added in 2 h at room temperature to a solution of $[\text{IrCl}(\text{COD})]_2$ (1.08 g, 1.61 mmol) in benzene (10 mL). Subsequent workup as described for 5 afforded orange-red 6 in 85% yield. Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{IrN}$: C, 47.0; H, 5.6; N, 3.2. Found: C, 45.6; H, 5.5; N, 3.0.

Synthesis of $\text{Ir}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,4}](\text{COD})$ (7). The procedure is analogous to that of 4, except that after the addition of the aryllithium compound to $[\text{IrCl}(\text{COD})]_2$, the hexane reaction mixture was refluxed for 5 min. After workup this affords orange-red 7 in 90% yield. Anal. Calcd for $\text{C}_{20}\text{H}_{31}\text{IrN}_2$: C, 48.9; H, 6.4; N, 5.7. Found: C, 47.1; H, 6.5; N, 5.3. Crystals suitable for an X-ray diffraction study were formed within 3 h by slow cooling of a warm saturated hexane solution of 7 to room temperature.

Synthesis of $\text{Ir}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2-Me-4}](\text{COD})$ (8). The procedure is analogous to that of 5, except that after the addition of the aryllithium compound to $[\text{IrCl}(\text{COD})]_2$, the benzene reaction mixture was heated to 60 °C for 1 h before workup. Yield: 75%.

Synthesis of $\text{Ir}[\text{C}_6\text{H}_2(\text{CH}_2\text{NMe}_2)_3\text{-2,4,6}](\text{COD})$ (9). To a solution of 2-Br-1,3,5-(Me_2NCH_2) C_6H_2 ⁵ (0.60 g, 1.8 mmol) in hexane (5 mL) was added *n*-BuLi (1.4 mL of a 1.35 M solution in hexane). The yellow solution of the aryllithium compound was then added to a suspension of $[\text{IrCl}(\text{COD})]_2$ (0.46 g, 0.69 mmol) in hexane (5 mL). Workup as for 4 afforded orange-red 9 in 80% yield.

Synthesis of $\text{Ir}[\text{C}_6\text{D}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}](\text{COD})$ (4-*d*₃). A mixture of 2-bromo-1,3-dimethylbenzene (5 g), D_2SO_4 (3.5 mL), and D_2O (4 mL) was refluxed for 5 days. After that time ¹H NMR measurements showed 78% deuterium enrichment of the three aryl hydrogens. The reaction mixture was diluted with water and extracted with CCl_4 (25 mL). This extract was used without further purification for the successive synthesis of 2-bromo-1,3-

(5) 2-Br-1,3,5-(Me_2NCH_2) C_6H_2 was synthesized from 2-Br-1,3,5-(BrCH_2) C_6H_2 and an excess of anhydrous Me_2NH in benzene.

Table I. Crystal Data and Details of the Structure Determination of $\text{Ir}^1[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,4}](\text{COD})$

a. Crystal Data	
formula	$\text{C}_{20}\text{H}_{31}\text{N}_2\text{Ir}$
mol wt	491.68
cryst system	monoclinic
space group	$\text{C}2/c$
<i>a</i> (Å)	23.829 (2)
<i>b</i> (Å)	11.667 (2)
<i>c</i> (Å)	13.725 (1)
β (deg)	93.43 (1)
<i>V</i> (Å ³)	3808.9 (8)
<i>Z</i>	8
<i>D</i> _{calcd} (g cm ⁻³)	1.715
<i>F</i> (000) (electrons)	1936
μ (Mo K α) (cm ⁻¹)	70.0
min and max absorptn correctn	0.838, 1.287
cryst size (mm)	0.3 × 0.3 × 0.3
b. Data Collection	
radiatn, Å	Zr-filtered Mo K α , $\lambda = 0.71073$
<i>T</i> , K	295
θ_{min} , θ_{max} (deg)	0.1, 27.5
$\omega/2\theta$ scan (deg)	$\Delta\omega = 0.60 + 0.35 \tan \theta$
data set	$-30 \leq h \leq 30, 0 \leq k \leq 15, 0 \leq l \leq 17$
ref reflectns	800, $\bar{2}04$, 040
total unique data	4368
obsd data (<i>I</i> > 2.5 σ (<i>I</i>))	3087
c. Refinement	
no. of refined parameters	234
weighting scheme	$w^{-1} = \sigma^2(F)$
final <i>R</i> , <i>wR</i> , <i>S</i>	0.026, 0.020, 3.05
min and max resid. density (e Å ⁻³)	-0.71, 0.67
(Δ/σ) _{max}	0.4

bis(bromomethyl)benzene-*d*₃ and 2-bromo-1,3-bis((dimethylamino)methyl)benzene-*d*₃. $\text{Ir}[\text{C}_6\text{D}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}](\text{COD})$ (4-*d*₃) was synthesized as described above for its nondeuterated analogue.

Thermal Conversion of $\text{Ir}[\text{C}_6\text{D}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}](\text{COD})$ (4-*d*₃). Complex 4-*d*₃ was heated in benzene and converted quantitatively to 7-*d*₃. The benzene was then removed in vacuo, whereupon CD_2Cl_2 or CH_2Cl_2 was added to the residue. Subsequent ¹H, ²H, and ¹³C NMR measurements of the resulting solutions confirmed the identity of 7-*d*₃ and showed it to be the only product in solution. ¹H NMR (CD_2Cl_2): as for 7 (see Table III), except that the two AB doublets at 6.89 and 7.09 ppm [attributed to the aromatic hydrogens at C(5) and C(6)] are absent. ²H NMR (CH_2Cl_2): δ 6.98 (aromatic hydrogens), 2.62 (coordinated NMe_2 group) with intensity ratio 2:1. ¹³C[¹H] NMR (CD_2Cl_2): as for 7 (see Table IV), except that the singlet signal at 50.2 ppm (attributed to a coordinated NMe_2 group) is partly split into a 1:1:1 triplet [¹J(¹³C-²H) = 21 Hz].

Kinetic Experiments. A. The conversions of 4 to 7 and of 5 to 8 were monitored by ¹H NMR at 47, 56, and 60 °C (0.2 M solutions in benzene-*d*₆) and for 4 at 56 °C only in the concentration range 0.03–0.2 mol/L. The conversion rates were obtained by following the decrease of the intensities of the benzylic CH_2 singlet signals. The rearrangements for both 4 and 5 were found to exhibit first-order kinetics with half-lives of 30 min at 56 °C and with $\Delta G^\ddagger = 24.5$ kcal/mol.

B. The methanolysis reactions of $\text{Ir}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2-R-4/6}](\text{COD})$ (4–8) with an excess of methanol-*d*₄ in benzene-*d*₆ under N_2 atmosphere were monitored by ¹H NMR at 25 °C. The reaction rates were obtained by following the relative decrease of the intensities of the CH_2NMe_2 signals in 4–8 with respect to the consecutive increase of the corresponding signals of the reaction product 1-R-3-(Me_2NCH_2) $\text{C}_6\text{H}_2\text{D}$ (see eq 2, vide infra). The reaction was found to exhibit pseudo-first-order kinetics in the iridium complex. Under these conditions the half-lives of 4 and 5 (*t*₁) were unmeasurably short (<1 s) and those of 6–8 (*t*₂) all had a value of ca. 3 days. With use of the Arrhenius equation, this corresponds approximately to an energy difference, $\Delta\Delta G^\ddagger = RT \ln(t_2/t_1)$, of at least 7.5 kcal/mol between the ΔG^\ddagger 's of the methanolysis reactions of 4 and 5 and 6–8.

Structure Determination and Refinement of $\text{Ir}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,4}](\text{COD})$ (7). Crystal data and numerical details

Table II. Positional and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms of $\text{Ir}^I[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-}2,4](\text{COD})$

atom	x	y	z	$U_{\text{eq}}^a, \text{\AA}^2$
Ir(1)	0.31468 (1)	0.13551 (1)	0.14533 (1)	0.0401 (1)
N(1)	0.2472 (1)	0.2470 (3)	0.1852 (2)	0.043 (1)
N(2)	0.0841 (2)	-0.1708 (3)	-0.0992 (3)	0.066 (1)
C(1)	0.2475 (2)	0.0490 (4)	0.0802 (3)	0.039 (1)
C(2)	0.1958 (2)	0.1076 (3)	0.0803 (3)	0.042 (1)
C(3)	0.1448 (2)	0.0556 (4)	0.0515 (3)	0.051 (1)
C(4)	0.1427 (2)	-0.0566 (4)	0.0191 (3)	0.050 (1)
C(5)	0.1931 (2)	-0.1138 (4)	0.0140 (3)	0.048 (2)
C(6)	0.2445 (2)	-0.0632 (4)	0.0441 (3)	0.043 (1)
C(7)	0.1994 (2)	0.2315 (4)	0.1110 (3)	0.048 (2)
C(8)	0.2601 (2)	0.3723 (4)	0.1928 (3)	0.059 (1)
C(9)	0.2288 (2)	0.2047 (4)	0.2798 (3)	0.052 (2)
C(10)	0.0878 (2)	-0.1142 (4)	-0.0062 (3)	0.068 (2)
C(11)	0.0352 (2)	-0.2444 (5)	-0.1090 (4)	0.092 (2)
C(12)	0.0839 (2)	-0.0884 (5)	-0.1785 (4)	0.086 (2)
C(13)	0.3746 (2)	0.0492 (4)	0.0656 (4)	0.052 (2)
C(14)	0.3697 (2)	-0.0064 (4)	0.1562 (4)	0.055 (2)
C(15)	0.4141 (2)	0.0023 (5)	0.2418 (4)	0.076 (2)
C(16)	0.4027 (2)	0.0999 (5)	0.3103 (4)	0.083 (2)
C(17)	0.3718 (2)	0.2002 (5)	0.2613 (3)	0.062 (2)
C(18)	0.3866 (2)	0.2500 (4)	0.1732 (4)	0.062 (2)
C(19)	0.4376 (2)	0.2147 (4)	0.1180 (4)	0.069 (2)
C(20)	0.4234 (2)	0.1238 (4)	0.0415 (4)	0.067 (2)

$$^a U_{\text{eq}} = \frac{1}{3} \sum_{ij} U_{ij} a_i^* a_j^* a_i \cdot a_j$$

of the structure determination are listed in Table I. X-ray data were collected on an Enraf-Nonius CAD4F diffractometer for an orange-brown transparent crystal mounted in a Lindemann glass capillary. Unit-cell parameters were derived by least squares from the diffractometer settings of 12 reflections^{6a} in the range $11 < \theta < 14^\circ$. The three reference reflections showed a linear decay of 6% over 70 h of X-ray exposure time. The standard deviations in the intensities based on counting statistics were increased according to an analysis of the variance of the reference reflections:^{6b} $\sigma^2(I) = \sigma_{\text{cs}}^2(I) + (0.007I)^2$. Data were corrected for the decay and L_p effects. Absorption correction was applied after convergence of the isotropic refinement ($R = 0.073$) according to the empirical correction method described by Walker and Stuart^{6c} (range of corrections: 0.838–1.287). The structure was solved with standard Patterson methods and refined on F by blocked full-matrix least-squares techniques. Hydrogen atoms were introduced at calculated positions [$d(\text{C-H}) = 1.08 \text{ \AA}$] and refined with fixed geometry with respect to their carrier atoms. The refined parameter set included a scale factor, the coordinates of the non-hydrogen atoms, their anisotropic thermal parameters, and two common isotropic temperature factors for the methyl and non-methyl group H atoms, respectively. Final positional parameters are listed in Table II. Scattering factors were taken from ref 6d and 6f and corrected for anomalous dispersion.^{6e} The calculations were carried out on the in-house Eclipse S/230 minicomputer with a locally modified version of the SHELX76 package^{6g} or the CYBER-855 of the University of Utrecht with programs of the EUCLID package^{6h} (calculation of geometrical data and preparation of illustrations).

Results

Synthesis and Characterization of $\text{Ir}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-}2\text{-R-}6](\text{COD})$ (4–6). The new iridium(I)

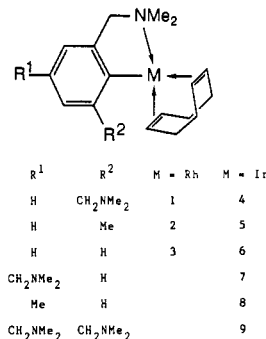
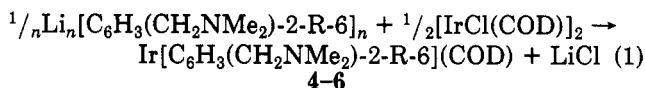


Figure 3. Solid-state structures of $\text{M}^I[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-}2\text{-R}^1\text{-}4\text{-R}^2\text{-}6](\text{COD})$ (1–9).

compounds $\text{Ir}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-}2\text{-R-}6](\text{COD})$ [$\text{R} = \text{CH}_2\text{NMe}_2$ (4), Me (5), and H (6)] were prepared in 85% yield from the reaction of $\text{Li}_n[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-}2\text{-R-}6]_n$ with $[\text{IrCl}(\text{COD})]_2$ according to eq 1.



The orange-red compounds 4–6 are, like their rhodium(I) analogues 1–3, soluble in benzene, toluene, and dichloromethane. They can be stored for months without apparent decomposition if kept at 0°C in an inert atmosphere. On exposure to air they all react rapidly with oxygen, as is evidenced by a striking color change from orange to blue-green.³

The structures of 4–6 (see Figure 3), as deduced from ^1H and ^{13}C NMR data (Tables III and IV), are similar to those of the rhodium analogues 1–3. (The X-ray structure of 1 is known³ and is shown in Figure 1.) They are thus square-planar iridium(I) complexes, with bidentate COD and (C,N-coordinated) aryl ligands. The ^1H and ^{13}C NMR spectra of 4–6 at 25°C show two resonances for the olefinic atoms of the COD moiety, consistent with the presence of a trans-C and a trans-N double bond.

As observed for the analogous rhodium(I) complex 1, only at low temperature does the NMR spectra of $\text{Ir}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-}2,6](\text{COD})$ (4) exhibit a pattern that is in accord with a C,N-bidentate coordination mode of the aryl ligand. Above -44°C in CD_2Cl_2 (ca. -80°C in toluene- d_6) the signals of the coordinated and uncoordinated CH_2NMe_2 groups coalesce, consistent with interchange of these two groups. The fluxional process can be explained as being a result of dissociation of the Ir–N bond and subsequent rotation of the aryl moiety around Ir–C(aryl) (Figure 2). The process is induced by repulsions between the trans-N double bond of COD and the CH_2 part of the 6-position aryl substituent.³ Consequently, when this latter substituent is replaced by a methyl group (as in 5), this repulsion will be similar and 5 as anticipated will also exhibit this type of fluxionality. Obviously, the steric hindrance in 4 and 5 is relieved upon rotation of the aryl ligand and its ortho substituents out of the coordination plane. At higher temperatures the two olefinic groups of COD in 4 and 5 remain inequivalent, and therefore the fluxional process is, just as for 1 and 2, attended by the intermediacy of a three-coordinate, T-shaped, 14-electron species. In this intermediate the 2- and 6-position substituents of the aryl group are now placed above and below the plane defined by iridium, C(aryl), and the midpoints of the two double bonds of COD (see Figure 2).

With NOE experiments, it was found that the complex $\text{Ir}[\text{C}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2\text{-}2](\text{COD})$ (6), like its rhodium(I) analogue 3, is nonfluxional. Then at room temperature, saturation of the trans-N olefinic protons of the COD

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Table III. ^1H NMR Data of 4-9^a

compound	solvent	<i>T</i> (°C)	aryl ^b	CH ₂ ^c	NMe ^c	=CH(COD) ^d
Ir[C ₆ H ₃ (CH ₂ NMe ₂) ₂ -2,6](COD) (4)	CD ₂ Cl ₂	+25	7.00 (m, 3 H)	3.66 (4 H)	2.37 (12 H)	3.66 (2 H) 4.61 (2 H)
	CD ₂ Cl ₂	-55	7.00 (m, 3 H)	3.00 (2 H) 4.04 (2 H)	2.04 (6 H) 2.51 (6 H)	3.61 (2 H) 4.44 (2 H)
	toluene- <i>d</i> ₈	+25	7.32 (m, 1 H) 7.42 (m, 2 H)	3.79 (4 H)	2.32 (12 H)	3.63 (2 H) 5.30 (2 H)
Ir[C ₆ H ₃ (CH ₂ NMe ₂) ₂ -2-Me-6](COD) ^e (5)	CD ₂ Cl ₂	+25	6.74 (m, 1 H) 6.86 (m, 1 H) 7.00 (m, 1 H)	4.08 (2 H)	2.57 (6 H)	3.67 (2 H) 4.48 (2 H)
	CD ₂ Cl ₂	+25	6.95 (m, 1 H) 6.99 (m, 1 H) 7.16 (m, 1 H) 7.24 (m, 1 H)	4.02 (2 H)	2.68 (6 H)	3.75 (2 H) 3.79 (2 H)
Ir[C ₆ H ₃ (CH ₂ NMe ₂) ₂ -2,4](COD) (7)	CD ₂ Cl ₂	+25	6.89 (m, 1 H) 7.09 (m, 1 H) 7.18 (1 H)	3.28 (2 H) 4.01 (2 H)	2.14 (6 H) 2.69 (6 H)	3.74 (2 H) 3.78 (2 H)
	toluene- <i>d</i> ₈	+25	7.41 (m, 1 H) 7.51 (1 H) 7.67 (m, 1 H)	3.62 (2 H) 3.70 (2 H)	2.30 (6 H) 2.44 (6 H)	3.72 (2 H) 4.38 (2 H)
	CD ₂ Cl ₂	+25	6.83 (m, 1 H) 7.07 (m, 1 H) 7.08 (1 H)	4.00 (2 H)	2.69 (6 H)	3.71 (2 H) 3.79 (2 H)
Ir[C ₆ H ₂ (CH ₂ NMe ₂) ₃ -2,4,6](COD) (9)	CD ₂ Cl ₂	+25	6.93 (2 H)	3.28 (2 H) 3.64 (4 H)	2.15 (6 H) 2.36 (12 H)	3.64 (2 H) 4.63 (2 H)
	CD ₂ Cl ₂	-60	6.70 (1 H) 7.00 (1 H)	3.04 (2 H) 3.21 (2 H) 4.07 (2 H)	2.08 (12 H) 2.55 (6 H)	3.64 (2 H) 4.46 (2 H)
	toluene- <i>d</i> ₈	+25	7.47 (2 H)	3.63 (2 H) 3.82 (4 H)	2.35 (12 H) 2.43 (6 H)	3.63 (2 H) 5.31 (2 H)

^a Measured at 250 MHz. Chemical shifts in ppm relative to external TMS. ^b For resolved AB₂ or AB pattern: ²*J*(H-H) = 8 Hz. ^c The high-field singlet corresponds to a coordinated CH₂NMe₂ group. ^d Broad resonances. ^e Aryl Me: 2.27 ppm. ^f Aryl Me: 2.41 ppm.

Table IV. ^{13}C NMR Data of 4-9^a

compd	aryl				CH ₂	NMe	=CH	CH ₂ (COD)
	C(1)	C(2,6)	C(3,5)	C(4)				
Ir[C ₆ H ₃ (CH ₂ NMe ₂) ₂ -2,6](COD) (4)	168.1	149.2	124.5	124.8	70.2	47.7	57.0	29.9
							71.4	33.3
Ir[C ₆ H ₃ (CH ₂ NMe ₂) ₂ -2-Me-6](COD) ^b (5)	167.4	150.0	125.0	128.3	74.9	49.4	56.6	29.3
		148.1	119.3				71.5	33.2
Ir[C ₆ H ₄ (CH ₂ NMe ₂) ₂](COD) (6)	166.8	151.5	125.2	128.9	75.7	50.2	57.2	30.9
		133.9	121.4				74.5	32.0
Ir[C ₆ H ₃ (CH ₂ NMe ₂) ₂ -2,4](COD) (7)	165.4	151.6	126.2	139.7	64.8	45.4	57.0	30.8
		133.8	122.3		75.7	50.2	74.2	31.9
Ir[C ₆ H ₃ (CH ₂ NMe ₂) ₂ -2-Me-4](COD) ^c (8)	163.6	151.8	126.0	<i>d</i>	75.9	50.3	57.0	31.0
		134.1	122.2				73.7	32.0
Ir[C ₆ H ₂ (CH ₂ NMe ₂) ₃ -2,4,6](COD) (9)	<i>d</i>	150.4	126.4	140.7	65.2	45.6	57.5	29.9
					69.4	47.4	70.3	33.8

^a Measured in CD₂Cl₂ at +25 °C and 25.18 MHz. Chemical shifts in ppm relative to external TMS. ^b Aryl Me: 24.3 ppm. ^c Aryl Me: 21.5 ppm. ^d Not observed.

moiety enhances the signal of the 6-position aromatic proton in 6. Similarly enhanced signals, of the 6-position alkyl substituents, were not seen in the fluxional complexes 4 and 5.

Syntheses and Characterization of Ir[C₆H₃(CH₂NMe₂)₂-2-R-4](COD) (7 and 8). The iridium(I) compounds 4 and 5 are unstable and can be thermally converted into the isomeric complexes 7 and 8, respectively, in which the alkyl substituent (i.e. CH₂NMe₂ in 4/7 and Me in 5/8) seems to have migrated from the 6- to the 4-position in the aryl ligand (Figure 4). The isomerized products could be obtained in good yield if the initial reaction mixture of Li_{*n*}[C₆H₃(CH₂NMe₂)₂-2-R-6]_{*n*} and [Ir-Cl(COD)]₂ in hexane or benzene was heated to 60–70 °C for a short time before workup. Accordingly, the irreversible conversion of 4 to 7, and 5 to 8, must be a very regioselective process.

The identities of 7 and 8 were deduced from ^1H and ^{13}C NMR data. The spectral features of 7 and 8 in toluene-*d*₈ were unaltered between -80 and +105 °C, indicating that, in contrast to their respective precursors 4 and 5, they have

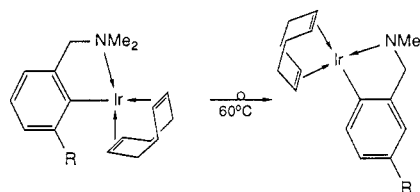


Figure 4. Thermal conversion of Ir^I[C₆H₃(CH₂NMe₂)₂-2-R-6](COD) to Ir^I[C₆H₃(CH₂NMe₂)₂-2-R-4](COD) (R = CH₂NMe₂, 4 to 7; R = Me, 5 to 8).

static, *nonfluxional* structures. The ^1H and ^{13}C resonances of both the COD ligand and (one of) the CH₂NMe₂ group(s) are virtually identical with those of complex 6 (see Tables III and IV), and consequently one can conclude that the iridium coordination spheres are very similar. In the ^1H NMR spectra of 7 and 8 the three aromatic protons afford an AB pattern and a singlet, consistent with a 1,2,4-substituted benzene ring. Consequently, the non-coordinating alkyl group (CH₂NMe₂ in 7, Me in 8) must be in the 4-position. For confirmation of these deduced

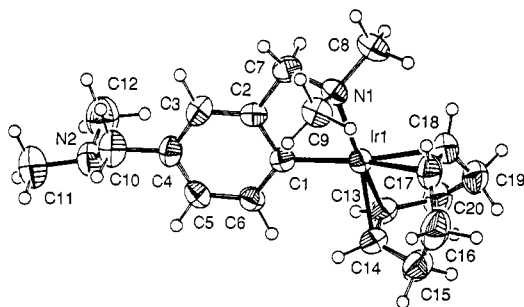


Figure 5. X-ray structure of $\text{Ir}^{\text{I}}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,4}](\text{COD})$ (**7**) showing thermal ellipsoids (50% probability) and adopted numbering scheme.

Table V. Selected Bond Distances (Å) of $\text{Ir}^{\text{I}}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,4}](\text{COD})^a$

(a) Around Iridium			
$\text{Ir}(1)\text{-N}(1)$	2.164 (3)	$\text{Ir}(1)\text{-C}(17)$	2.167 (5)
$\text{Ir}(1)\text{-C}(1)$	2.052 (5)	$\text{Ir}(1)\text{-C}(18)$	2.188 (5)
$\text{Ir}(1)\text{-C}(13)$	2.106 (5)	$\text{Ir}(1)\text{-m}(1)$	1.988 (4)
$\text{Ir}(1)\text{-C}(14)$	2.112 (5)	$\text{Ir}(1)\text{-m}(2)$	2.061 (4)
(b) Within Aryl Ligand			
$\langle\text{N}(1)\text{-C}\rangle$	1.489 (7)	$\text{C}(2)\text{-C}(7)$	1.507 (6)
$\langle\text{N}(2)\text{-C}\rangle$	1.444 (7)	$\text{C}(4)\text{-C}(10)$	1.493 (7)
		$\langle\text{C}(\text{sp}^2)\text{-C}(\text{sp}^2)\rangle$	1.39 (1)
(c) Within COD Ligand			
$\text{C}(13)\text{-C}(14)$	1.414 (8)	$\langle\text{C}(\text{sp}^2)\text{-C}(\text{sp}^3)\rangle$	1.52 (1)
$\text{C}(17)\text{-C}(18)$	1.405 (7)	$\langle\text{C}(\text{sp}^3)\text{-C}(\text{sp}^3)\rangle$	1.514 (5)

^am(1) is the midpoint of C(13)–C(14); m(2) is the midpoint of C(17)–C(18).

structures, the molecular geometry of **7** has been determined by a single-crystal X-ray diffraction analysis.

Solid-State Structure of $\text{Ir}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,4}](\text{COD})$ (7**).** The monoclinic unit-cell contains eight discrete molecules of **7**. The molecular structure and the adopted numbering scheme of **7** is shown in Figure 5. Selected bond distances and angles are listed in Tables V and VI, respectively. The complex has a square-planar configuration in which the iridium center is surrounded by the double bonds of COD [$\text{C}(13)=\text{C}(14)$ and $\text{C}(17)=\text{C}(18)$] with midpoints m(1) and m(2), respectively] and by the aryl ligand through C(1) of the ring and N(1) of the 2- CH_2NMe_2 group. The iridium atom lies only 0.05 (1) Å out of the plane defined by C(1), N(1), m(1), and m(2). The bidentate C,N-coordination of the aryl ligand to iridium gives rise to an acute C(1)–Ir(1)–N(1) angle of 80.4 (2)° and departure of the angles around C(1) from a pure trigonal geometry [$\text{Ir}(1)\text{-C}(1)\text{-C}(6)$ is enlarged to 129.5 (4)°, while the other angles are correspondingly smaller]. The $\text{Ir}(1)\text{-C}(1)$ length of 2.052 (5) Å, however, is normal.⁷ The orientation of the para-position noncoordinating CH_2NMe_2 group, manifested by the torsion angle C(5)–C(4)–C(10)–N(2) of –51.6 (6)°, is probably governed by crystal packing effects.

The COD ligand has the usual twisted boat conformation. The midpoints of the two coordinated double bonds of COD [m(1) and m(2)] make an angle of 87.1 (2)° with the iridium center. The distance of iridium to the double bond trans to C(aryl) [2.061 (5) Å] is longer than that trans to N [1.987 (5) Å], a difference which has also been observed in $\text{Rh}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}](\text{COD})$ (**1**) and which is ascribed to the higher trans influence of C(aryl).³

For the rhodium(I) complex **1** it was deduced that there was a severe intramolecular repulsion between the atoms

Table VI. Selected Bond Angles (deg) of $\text{Ir}^{\text{I}}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,4}](\text{COD})^a$

(a) Around Iridium			
$\text{N}(1)\text{-Ir}(1)\text{-C}(1)$	80.4 (2)	$\text{C}(1)\text{-Ir}(1)\text{-m}(1)$	95.6 (2)
$\text{N}(1)\text{-Ir}(1)\text{-m}(1)$	174.9 (1)	$\text{C}(1)\text{-Ir}(1)\text{-m}(2)$	176.6 (1)
$\text{N}(1)\text{-Ir}(1)\text{-m}(2)$	96.8 (1)	$\text{m}(1)\text{-Ir}(1)\text{-m}(2)$	87.0 (2)
(b) Within Aryl Ligand			
$\langle\text{C-N}(1)\text{-C}\rangle$	108.4 (8)	$\text{Ir}(1)\text{-C}(1)\text{-C}(2)$	114.9 (3)
$\langle\text{C-N}(2)\text{-C}\rangle$	111.0 (2)	$\text{Ir}(1)\text{-C}(1)\text{-C}(6)$	129.5 (4)
$\text{Ir}(1)\text{-N}(1)\text{-C}(7)$	107.6 (2)	$\text{C}(2)\text{-C}(1)\text{-C}(6)$	115.3 (4)
$\text{Ir}(1)\text{-N}(1)\text{-C}(8)$	116.9 (2)	$\text{N}(1)\text{-C}(7)\text{-C}(2)$	109.6 (4)
$\text{Ir}(1)\text{-N}(1)\text{-C}(9)$	106.6 (3)	$\text{N}(2)\text{-C}(10)\text{-C}(4)$	114.9 (4)
(c) Within COD Ligand			
$\langle\text{C}(\text{sp}^2)\text{-C}(\text{sp}^2)\text{-C}(\text{sp}^3)\rangle$	124.0 (3)		
$\langle\text{C}(\text{sp}^2)\text{-C}(\text{sp}^3)\text{-C}(\text{sp}^3)\rangle$	113.1 (6)		

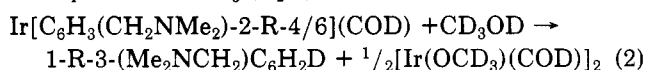
^am(1) is the midpoint of C(13)–C(14); m(2) is the midpoint of C(17)–C(18).

of the trans-N double bond and those of the methylene group of the adjacent 6-position CH_2NMe_2 substituent of the aryl ligand (see Figure 1). In the present iridium complex **7**, however, such a repulsion does not exist because the 6-position substituent is a sterically undemanding H atom. This difference in intramolecular steric crowding between **1** (cf. **4**) and **7** is crucial when the driving force for the conversion of **4** to **7** and also of **5** to **8** is discussed.

Conversion of $\text{Ir}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-R-6}](\text{COD})$ to $\text{Ir}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-R-4}](\text{COD})$ (4** to **7** and **5** to **8**).** **Characteristics and Thermodynamics.** In summary, the **4** to **7** and **5** to **8** conversions are induced thermally at ca. 60 °C in either hexane, benzene, toluene, or acetonitrile and are irreversible. These thermal conversions proceed very selectively because no products other than complexes **7** and **8** were found after the rearrangements of **4** and **5**, respectively, had occurred. Furthermore, when these conversions were monitored by ¹H NMR, no intermediates were observed. Looking at it from the point of view of substituents on the aryl ring, the net result of the conversion can be envisaged as the exchange of the 1-position Ir(COD) moiety with the 3-position hydrogen atom. An alternative description, involving the exchange of the 6-position, noncoordinating R group (R = CH_2NMe_2 in **4** and Me in **5**) with the 4-position hydrogen atom, would involve the highly improbable rupture of a C–C bond and can therefore be disregarded.

A major point of interest concerns the thermodynamics of the conversions. Obviously, compounds **7** and **8** are thermally more stable than their precursors **4** and **5**, and consequently the process is exothermic. For $\text{Ir}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-R-6}](\text{COD})$ (**4** and **5**) it was concluded that, as for their rhodium(I) analogues **1** and **2**, severe repulsions exist between the COD and aryl ligand, especially between the trans-N double bond and the adjacent 6-position alkyl group (CH_2NMe_2 in **4**, Me in **5**). In the isomerized products **7** and **8**, such repulsions involving this R group are now absent, and this difference provides the driving force for the conversion.

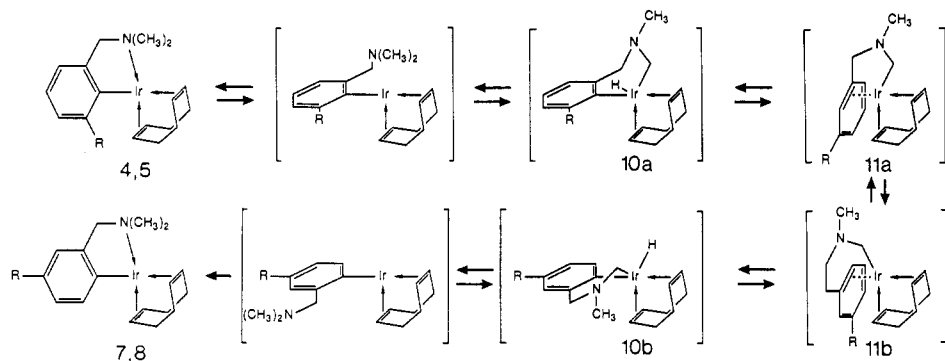
An estimate of the energy difference between the sterically hindered complexes **4** and **5** and the nonsterically hindered ones **6–8** can be made by measuring the rate of the reaction of these iridium(I) complexes with methanol-*d*₄ in benzene-*d*₆ (eq 2). It was found that whereas



complexes **6–8** had a half-life of 3 days, **4** and **5** reacted within less than one second. With use of these values, an energy difference $\Delta\Delta G^\ddagger$ of at least 7.5 kcal/mol can be

(7) Clearfield, A.; Gopal, R.; Bernal, I.; Moser, G. A.; Rausch, M. D. *Inorg. Chem.* 1975, 14, 2727.

Scheme I. Postulated Mechanism for the Conversion of Ir^I[C₆H₃(CH₂NMe₂)₂-2-R-6](COD) [R = CH₂NMe₂ (4), Me (5)] to Ir^I[C₆H₃(CH₂NMe₂)₂-2-R-4](COD) [R = CH₂NMe₂ (7), Me (8)]



calculated between the ΔG^\ddagger 's of the methanolysis reactions of 4 and 5 and 6–8. If the methanolysis would occur via the four-coordinate species, such a difference in reaction rate would not be expected. It seems therefore plausible that for both 4 and 5 and 6–8 this reaction requires the formation of a vacant coordination site at Ir, i.e. the formation of the T-shaped intermediate. Accordingly, this energy difference can be assumed to mainly arise from the difference in Ir–N dissociation rate and hence in the difference in repulsion between the complexes 4 and 5 on one hand and 6–8 on the other. Then $\Delta\Delta G^\ddagger$ would correspond to the energy lost, and hence the driving force, for the conversions of 4 and 5 to 7 and 8, respectively.

Deuterium Studies. As the aryl ligand changes from a 1,2,3-substituted aryl group in 4 and 5 to a 1,2,4-substituted one in 7 and 8, the rearrangement must involve the breaking and making of at least one C(aryl)–H bond. Therefore, the conversion must include a C–H oxidative addition (reductive elimination) step at the metal center. Experiments were thus carried out to determine whether this step was accomplished by complexes 4 and 5 (intra- or intermolecular) or by solvent molecules.

When the conversions were carried out in benzene-*d*₆ or toluene-*d*₈, no deuterium uptake in 7 or 8 was found either at the position of the former C(aryl)–Ir bond or elsewhere. Oxidative addition of solvent C–H(D) bonds to 4 and 5 in the rearrangement process were thus ruled out. Furthermore, measurements on the conversions in benzene-*d*₆ show that the rate-determining step in the rearrangement has first-order kinetics ($\Delta G^\ddagger = 24.5$ kcal/mol; see Experimental Section), and this is indicative of an intramolecular rather than an intermolecular process. To identify which of the C–H bonds is actually involved in the intramolecular rearrangement, Ir[C₆D₃(CH₂NMe₂)₂-2,6](COD) (4-*d*₃) was synthesized, with the three aromatic hydrogens having a 78% deuterium enrichment. The thermal conversion of 4-*d*₃ to 7-*d*₃ was then investigated by ¹H, ²H, and ¹³C NMR. It was found that the isomerization resulted in incorporation of deuterium into the Me groups of the coordinated CH₂NMe₂ substituent of 7-*d*₃ and in the formation of a C–H bond at the former C(aryl)–Ir site (Figure 6). This implies that the proton of the newly formed C(aryl)–H bond of 7-*d*₃ comes from one of the four (non-deuteriated) NMe groups of 4-*d*₃ and that the deuterium in the NMe₂ group of 7-*d*₃ comes from the former 3-position C(aryl)–D bond of 4-*d*₃.

The Mechanism. On the basis of the above results, the mechanism of the conversion of 4 to 7 and of 5 to 8 has been deduced and is depicted in Scheme I. The consecutive steps will now be discussed in detail.

The first, and probably rate-determining, step in the conversion is the oxidative addition of an aliphatic C–H

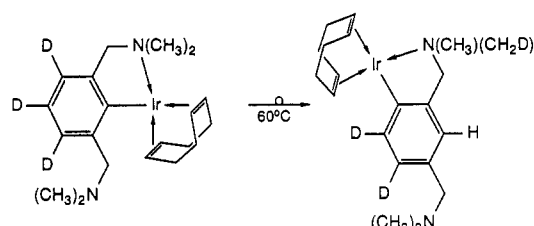


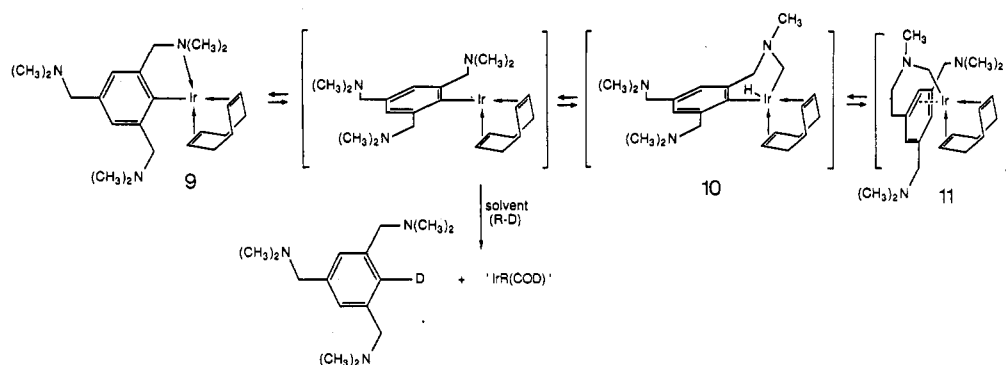
Figure 6. Thermal conversion of 4-*d*₃ to 7-*d*₃.

bond of one of the NMe groups in 4 or 5 to the iridium(I) center. Note that the addition can only occur with the three-coordinate, T-shaped, 14-electron configuration of 4 or 5 because a C–H bond of the NMe group can only approach the metal center when the adjacent nitrogen atom is not coordinated to it. This first (cyclometallation) step results in the formation of a 1-irida-3-azatetralin derivative (10a), a six-membered aryl–alkyl metallacycle hydride with a five-coordinate, 16-electron iridium(III) center.

In the second step, the intermediate 10a now has a choice for further reaction via (i) reductive elimination of a C(alkyl)–H bond, re-forming 4/5, or (ii) reductive elimination of a C(aryl)–H bond, resulting in the formation of a new intermediate (11a), or (iii) insertion of a COD double bond into the Ir–H bond. Although process i may occur, it is nonproductive, and, while there is no evidence that process iii occurs, process ii is the only productive pathway. Since process iii would be exothermic, and in view of the recent isolation of stable iridium(III) COD dihydrides,⁸ its absence is probably due to a high kinetic barrier.

It should be noted that reductive elimination of a C–H bond is usually an exothermic process,^{1a} with that of a C(alkyl)–H bond being thermodynamically more favorable than that of a C(aryl)–H bond because a metal–C(aryl) bond is stronger than a metal–C(alkyl) bond.⁹ The reason that process ii [C(aryl)–H reductive elimination] becomes favorable must, therefore, relate to the removal of the steric repulsion between the 6-substituent of the aryl ligand and the COD moiety or the hydride atom in 10a. Intermediate 11a, resulting from this second step, is an iridium(I) species in which the aryl ligand is now bonded to iridium through

(8) (a) Crabtree, R. H.; Felkin, H.; Fillebeen-Khan, T.; Morris, G. E. *J. Organomet. Chem.* 1979, 168, 183. (b) Crabtree, R. H.; Uriarte, R. J. *Inorg. Chem.* 1983, 22, 4152. (c) Kretschmer, M.; Pregosin, P. S.; Albinati, A.; Togni, A. *J. Organomet. Chem.* 1985, 281, 365. (d) Fernandez, M. J.; Esteruelas, M. A.; Oro, L. A.; Apreada, M.; Foces-Foces, C.; Cano, F. H. *Organometallics* 1987, 6, 1751. (e) van der Zeijden, A. A. H.; van Koten, G.; Luijk, R.; Grove, D. M. *Organometallics*, following paper in this issue. (9) Nolan, S. P.; Hoff, C. D.; Stoutland, P. O.; Newman, L. J.; Buchanan, J. M.; Bergman, R. G.; Yang, G. K.; Peters, K. S. *J. Am. Chem. Soc.* 1987, 109, 3143.

Scheme II. Thermal Decomposition of Ir^I[C₆H₂(CH₂NMe₂)₃-2,4,6](COD) (9) in Toluene-*d*₈

an Ir-C(alkyl) bond and probably also through an η^2 -arene-iridium bond. The latter bond seems necessary, since 11a would otherwise be a highly unsaturated three-coordinate species.

In the third step the Ir(COD) moiety in 11a migrates to a less sterically hindered position on the aryl ring to afford 11b. Such a haptotropic rearrangement along the aryl ring will have a low activation barrier.¹⁰ At this barrier we are now at the "midpoint" of the conversion and all subsequent steps are now those already discussed, but in reverse order: Thus, from 11b the fourth step is the oxidative addition of a C(aryl)-H bond at the less hindered, former 3-position, resulting in the formation of an aryl-alkyl metallacycle hydride, 10b analogous to 10a. This clearly indicates that the addition of the C(aryl)-H bond at this 3-position is much more favored than that of the 1-position, a difference that is solely governed by steric crowding of the R group. Intermediate 10b now has, like in 10a, the choice for reductive elimination of either the C(aryl)-H bond (the backward reaction) or the C(alkyl)-H bond. In contrast to 10a, the latter process occurs, presumably because this allows rapid subsequent complexation of the amine site of the aryl ligand, forming 7 or 8. Although all previous steps were potentially reversible, this final step is largely irreversible, and this drives the conversion to completion.

Discussion. The intramolecular rearrangement of 4 to 7 and of 5 to 8 is unique since it involves the highly regioselective making and breaking of four C-H bonds in a sequence. Although this conversion does not, as far as we are aware, have any close precedents in organometallic chemistry, the individual steps do have congeners. For example, hydride-containing metallacycles similar to 10 have been proposed as intermediates during the rearrangement of *cis*-Pt(CH₂CMe₂Ph)₂(PET₃)₂ to *cis*-Pt(CH₂CMe₂Ph)(C₆H₄-2-CMe₃)(PET₃)₂¹¹ and of Rh(CH₂CMe₂Ph)(PPh₃)₃ to Rh(C₆H₄-2-CMe₃)(PPh₃)₃,¹² in which metal-alkyl bonds are exchanged for metal-aryl bonds. They have also been proposed in several other cyclometalation reactions, such as that of azobenzene with MnMe(CO)₅,² or that of IrMe(PPh₃)₃ affording Ir(C₆H₄-2-PPh₂)(PPh₃)₂.¹³ Furthermore, stable species of this type are also known.¹²

To our knowledge there is only one example of a stable, isolated complex in which an aryl ligand is, as in intermediate 11, bonded via both a metal-alkyl bond and an arene π -bond.¹⁴ The presence of η^2 -arene-metal bonds

has been observed in the activation reactions of aromatic C-H bonds with CpML (M = Rh, Ir),^{1e-j} although it has been stated that this prior bonding is *not* a prerequisite for metalation.

Reactions Involving Ir[C₆H₂(CH₂NMe₂)₃-2,4,6](COD) (9). To study the effect of a third alkyl group at the 4-position of the aryl ligand on the activation of C-H bonds, Ir[C₆H₂(CH₂NMe₂)₃-2,4,6](COD) (9) was synthesized. Like 4, complex 9 exhibited the same fluxional process in toluene-*d*₈, involving the interchange of the 2- and 6-position CH₂NMe₂ groups arising from rotation of the aryl ligand about the Ir-C(aryl) bond. At 65 °C, a temperature at which 4 and 5 rapidly isomerize, there was still no reaction of 9 in toluene-*d*₈ (based on ¹H NMR observations). However, at ca. 80 °C the resonances of 9 begin to disappear in favor of those of the free arene 1,3,5-(Me₂NCH₂)₃C₆H₂D (quantitative degree of deuteriation derived from ¹H NMR integration), while at the same time the solution blackens (free Ir⁰). The monodeuterated arene end product is clearly the result of a reaction of 9 with the solvent toluene-*d*₈ (see Scheme II). It is anticipated that this reaction would be accompanied by the formation of "Ir(tolyl)(COD)", which is likely to decompose immediately under the prevailing conditions.¹⁵

As mentioned before, the driving force for the isomerizations of 4 to 7 and of 5 to 8 is the relief of steric crowding in 4 and 5. When a third CH₂NMe₂ group is introduced at the 4-position of the aryl ring (as in 9), the intermediates 10a and 10b as well as 11a and 11b in the isomerization process are identical (see Schemes I and II). Thus, although the rearrangement of 9 via the intermediates 10 and 11 will be entropically driven, the energy gain is zero. Therefore, since no exothermic reaction can be achieved by intramolecular C-H addition, intermolecular C-H addition (of the solvent) occurs as an alternative. It can also be deduced that, as no deuterium was incorporated in the NMe groups (as a possible result of the reaction of the intermediate 11 with toluene-*d*₈), the C(alkyl)-H oxidative addition/C(aryl)-H reductive elimination sequence in 9, via intermediates 10 and 11, is reversible.

Conclusions

The activation of C-H bonds by the present iridium(I) complexes can be carefully controlled by adjusting the steric bulk of the aryl ligands present. It has been shown that the direction of C-H activation processes can be substantially influenced by steric crowding around the metal center.

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Registry No. 4, 114762-89-9; 4-*d*₃, 114762-95-7; 5, 114762-90-2; 6, 114762-91-3; 7, 114762-92-4; 7-*d*₃, 114762-96-8; 8, 114762-93-5; 9, 114762-94-6; 2,6-(Me₂NCH₂)₂C₆H₃Br, 66479-06-9; [IrCl(COD)]₂,

12112-67-3; 1-Me-2-Br-3-(Me₂NCH₂)C₆H₃, 114739-32-1; Li₄[C₆H₄(CH₂NMe₂)₂]₄, 56174-66-4; 2-Br-1,3,5-(Me₂NCH₂)₃C₆H₂, 114739-29-6; 2-bromo-1,3-dimethylbenzene, 576-22-7; 2-bromo-1,3-dimethylbenzene-*d*₃, 114739-30-9; 2-bromo-1,3-bis((dimethylamino)methyl)benzene-*d*₃, 114739-31-0.

Supplementary Material Available: Lists of hydrogen atom positions and thermal parameters and complete lists of bond distances and angles (4 pages); a listing of the *F*_o and *F*_c values (25 pages). Ordering information is given on any current masthead page.

Formation of Octahedral Iridium(III) Dihydrides from the Reaction of Ortho-Chelated Aryliridium(I) Compounds with Dihydrogen

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The reaction of Ir^I[C₆H₂(CH₂NMe₂)₂-2-R¹-4-R²-6](COD) (COD = cycloocta-1,5-diene) with dihydrogen in CD₂Cl₂ was monitored by ¹H NMR. At -20 °C quantitative formation of the novel dihydride complexes Ir^{III}H₂[C₆H₂(CH₂NMe₂)₂-2-R¹-4-R²-6](COD) [R¹ = H, R² = CH₂NMe₂ (10), Me (11); R² = H, R¹ = H (12), Me (13), CH₂NMe₂ (14); R¹ = R² = CH₂NMe₂ (15)] occurs. Further reactions, the type of which depends on the bulkiness of the R¹ and R² groups, occur when these solutions are warmed to 0 °C. Complexes 12-14 (R² = H) lose H₂ to re-form Ir^I[C₆H₃(CH₂NMe₂)₂-2-R¹-4](COD). In contrast, complexes 10, 11, and 15 (R² = alkyl) react further by means of C(aryl)-H reductive elimination. For complex 15 (R¹ = CH₂NMe₂) this results in quantitative formation of 1,3,5-(Me₂NCH₂)₃C₆H₃ and "IrH(COD)". In Ir^{III}H₂[C₆H₃(CH₂NMe₂)₂-2-R-6](COD) [R = alkyl (10 and 11)], C(aryl)-H reductive elimination is followed by re-addition of another C(aryl)-H bond, which upon subsequent reductive elimination of H₂, yields the rearranged iridium(I) complexes Ir^I[C₆H₃(CH₂NMe₂)₂-2-R-4](COD). Since the rearrangement of Ir^I[C₆H₃(CH₂NMe₂)₂-2-R-6](COD) to Ir^I[C₆H₃(CH₂NMe₂)₂-2-R-4](COD) can also be induced thermally at 60 °C, it is therefore being catalyzed by dihydrogen at 0 °C. None of these reactions with dihydrogen is attended by hydrogenation of the COD ligand.

Introduction

The oxidative addition of dihydrogen to metal d⁸ complexes is a key step in homogeneous hydrogenation and hydroformylation catalysis.¹ Since the discovery of the first stable metal dihydrido olefin complexes in 1976 by Crabtree et al.,² several papers have emerged on the observation of other species of this type.³ These species, as well as recently isolated *cis*-alkyl/aryl/acyl hydride rhodium and iridium complexes,⁴ can be regarded as intermediates in the homogeneous catalytic hydrogenation of olefins.

In previous papers we reported the syntheses of M^I[C₆H₃(CH₂NMe₂)₂-2-R-6](COD) [M = Rh, R = CH₂NMe₂ (1), Me (2), H (3);⁵ M = Ir, R = CH₂NMe₂ (4), Me (5), H (6)] and Ir^I[C₆H₂(CH₂NMe₂)₃-2,4,6](COD) (9);⁶ see Figure 1. We also reported that compounds 4 and 5, which suffer from internal steric crowding between the 6-substituted alkyl group and the adjacent COD double bond, isomerize quantitatively in an unusual way to Ir^I[C₆H₃(CH₂NMe₂)₂-2-R-4](COD) [R = CH₂NMe₂ (7) and Me (8), respectively]. The mechanism of this conversion involves

the successive intramolecular breaking and making of several C-H bonds (see Scheme I). Some of the postulated intermediates in this conversion involve iridium(III) hydride species yet, despite the *cis* arrangement of the metal hydride and one of the double bonds of COD, no hydrogenation of COD was observed. In view of this it was anticipated that the reaction of molecular hydrogen with the iridium(I) complexes 4-9 might lead to isolable iridium(III) dihydride species. This paper contains the results

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